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ANALYTICAL PROCEDURES FOR INDUSTRIAL WASTES*

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In this discussion of the analysis of industrial wastes, consideration will be given to the over-all problems involved. There will be no elaboration of the details of any particular sampling, compositing or analytical procedure, or programming of the approach to any specific problem. Essentially, this discussion will be concerned with the logic and reasoning behind the selection and application of analyses for evaluation of the sanitary importance of a particular waste.

The analytical procedures which may be applied to industrial wastes can be divided roughly into three categories:

(1) The general sanitary criteria developed for the measurement and control of sewage treatment processes.

(2) Procedures established as an integral part of stream standards.

(3) Chemical procedures especially designed to fit a particular industrial waste.

In addition to these tests, an industrial waste may require

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special biological examination such as:

(1) Biological assay for toxicity to aquatic life, particularly studies of the toxicity of a waste to fish, or the food organisms which make fish life possible.

(2) Biological assay designed to evaluate the possible deleterious effect of a waste on sewage disposal processes or stream purification.

Such specialized biological assay is important, but this discussion will of necessity be limited to consideration of the first grouping of tests presented.

As background for elaboration of the testing of industrial wastes, it would be well to make some classification of industrial wastes. One of the many possible classification schemes is presented in Table 1. The classification presented is to some extent arranged on the basis of the appropriate analytical approach. The relationship of the grouping presented to suitable analytical techniques will develop as this discussion proceeds

Applicability of the General Sanitary Criteria to the Evaluation of Industrial Wastes

The term, "general sanitary criteria", has been devised to designate the long established parameters so generally used in the control of sewage treatment processes and as measures of the

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TABLE I

Types of Industrial Wastes

A. Wastes Principally Mineral in Nature

1. Brine wastes
2. Mine drainage
3. Waste slurries
4. Mineral washing slurries and suspensions
5. Pickle liquor wastes
6. Plating wastes
7. Miscellaneous wastes from inorganic chemical manufacture

B. Wastes that Contain Principally Organic Materials

I. Hydrocarbon Wastes

1. Oil wells
2. Petroleum refineries
3. Styrene manufacturing plants
4. Copolymer rubber plants
5. Butadiene manufacturing plants
6. Natural rubber processing or reclaiming
7. Gasoline filling stations, bulk stations, garages, etc.

II. Miscellaneous Organic Chemical Wastes

8. Munitions plants such as T.N.T. tetryl and ammonium picrate manufacture
9. Pharmaceuticals (Synthetic)
10. Synthetic fiber plants such as viscose or nylon
11. Organic chemical manufacture

III. Phenolic Wastes

12. Gas plants
13. By-product coke plants
14. Chemical plants
15. Synthetic resin plants (phenol resins)
16. Tar, road oil and creosoting plants
17. Wood distillation plants
18. Dye manufacturing plants

IV. Biological Wastes

a. Wastes from processing biological materials and/or from biological processes

19. Tanneries
20. Pharmaceuticals (Antibiotics, Biologicals)
21. Alcohol Industries (Breweries and Distilleries)
22. Miscellaneous fermentation industries
23. Glue and gelatin plants
24. Wool scouring
25. Textile manufacture
26. Paper manufacture, particularly sulfite pulp and Kraft mills
27. Laundry wastes

b. Food processing wastes

28. Canneries
29. Meat packing
30. Milk and dairy products plants
31. Corn products plants
32. Beet sugar plants
33. Cane sugar plants
34. Fish processing plants
35. Other food processing and dehydration plants

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sanitary condition of streams. These include biochemical oxygen demand (B.O.D.), oxygen consumed, nitrogen in various forms, the various determinations of solids and volatile matter, and alkalinity or acidity along with pH, temperature, dissolved oxygen, etc.

In general, these values will adequately describe the sanitary significance of food processing wastes (Group IV-b) and will, with minor modification serve to characterize the wastes listed in Group IV-a.

Frequently, the relationship of the B.O.D. test to the oxygen consumed value is not appreciated. It might be well to point out that these two values are complementary. In general, neither determination can be substituted for the other. The B.O.D. test is essentially a biological assay. It measures the amount of material in a medium which can be oxidized by biochemical agencies under stipulated conditions. On the other hand, the oxygen consumed test is a strictly chemical oxidation carried out under rigidly specified conditions.

There are a number of oxygen consumed tests which are in use. Many more have been proposed. A group of these tests is now undergoing evaluation by a Standard Methods committee of the Federation of Sewage Works Association. Without exception, every oxygen consumed test is a chemical oxidation made according to a fixed procedure.

Occasionally an enthusiastic chemist, after devising a new or improved oxygen consumed method, decides that his procedure gives the same information as is yielded by a B.O.D. test. Such a result seems most unlikely. In order for an O.C. (Oxygen Consumed) test to be the equivalent of a B.O.D. test, it must show nearly perfect correlation with the B.O.D. test.

Recently Moore, et al,[1] in evaluating an oxygen consumed procedure, studied the oxidation of a group of representative chemical compounds. This sort of work would represent one phase of the demonstration that an O.C. test is the equivalent of a B.O.D. test. With data such as are described above, it would be necessary to establish that all compounds chemically oxidized are also biologically oxidized and that no compound is chemically attacked which is not also biologically oxidized. The development of an O.C. test having such characteristics does not seem probable.

As an example, acetates and saturated straight chain fatty acids show a high degree of resistance to chemical oxidation, yet they are readily oxidized by microorganisms. On the other hand, cellulose, to cite one example, is most resistant to microorganisms in aerobic systems, yet it readily undergoes chemical oxidation. With these two common materials as criteria, any of the O.C. tests proposed to date can be classified as definitely not the equivalent of a B.O.D. test.

However, because there is frequently some correlation between an O.C. test and the B.O.D. test, the O.C. test has a definite sphere of usefulness. The advantages of the O.C. test may be delineated as follows:

(1) It can be used to secure results rapidly.
   (a) In some cases it may serve as a guide in selecting appropriate dilutions for B.O.D. tests.
(2) It may be used as an index on wastes containing toxic materials which cannot be satisfactorily examined by the B.O.D. test.
(3) In some cases, where equipment and necessary material for the B.O.D. test are not available, the use of an O.C. test may be necessary.
(4) On certain chemical wastes, the O.C. test is perhaps the best parameter available to measure the amount of material being discharged.

The general sanitary criteria frequently are not well adapted to characterizing a waste. It would obviously be useless to run B.O.D., nitrogen values or the like on most of the mineral wastes listed in Group "A", Table I. These materials can best be evaluated in terms of pH, acidity or alkalinity, solids and the determination of definite mineral constituents.

A group of determinations or examinations which may be

arbitrarily applied to industrial wastes are those procedures which are stipulated as an integral part of stream standards. When definite limits for the amounts or concentrations of certain materials which may be discharged are established, it is a practical administrative measure to specify in detail the means which shall be used to determine whether a waste conforms to the established standard. Further, the procedure specified actually becomes a definitive part of the standard. For instance, it would be possible to debate at great length regarding what constitutes "oil" in a waste. However, when a procedure for the determination of oil is adopted as part of a standard, the procedure so adopted serves as a clear definition of oil. For the purpose of interpreting the standard, oil is that material which is measured as oil by the procedure stipulated.

In reaching agreement on methods designed to become a part of stream standards, a perplexing problem frequently occurs. This is the difficulty which arises in trying to make a practical compromise between those methods or procedures which most closely approach technical perfection, and methods which can be carried out at reasonable cost. It is obviously undesirable to stipulate any method which the parties concerned cannot afford to use, either because of an excessive requirement in the way of man hours and laboratory space per determination, or because very expensive and highly specialized equipment is required.

In the tentative concentrations listed by the International Joint Commission as "Objectives for Boundary Waters Quality Control"(2) definite limits were established for the amount of certain materials which might be discharged. Many of the techniques prescribed for interpretation of the "Objectives" represent not the best procedure available, but the best procedure which it was deemed feasible to specify.

Under this heading of arbitrary procedures, as an example, the International Joint Commission(3) tentatively prescribed methods for phenolic material, pH, iron, and oil, as part of their "Objectives for Boundary Waters Quality Control". While some of these are determinations which have been designated as the general sanitary criteria, they assume a definite identity as part of a quality standard for wastes.

Finally, it is necessary to select or develop analyses designed to best characterize a particular waste. There are no inclusive simple rules which may be laid down for choosing the right group of analytical determinations to use. The experience, judgment, and "know-how" of the personnel involved must be used to the fullest extent.

Before undertaking the examination of most industrial wastes, the goal or purpose of the examination should be clearly established. Thus, one series of determinations might be pertinent if a given waste is suspected of causing taste and odor difficulties, a second group would be applicable if the

waste is being considered as a possible contributor to a serious oxygen sag, and a third group of determinations might best be used if the waste is believed to be a source of toxic metals or cyanides.

The value of the establishment of objectives in connection with the analyses of industrial wastes cannot be over emphasized. Once the objectives of the examination are thoroughly understood, the analyses have a definite goal. It is then possible to lay out a compact analytical program which will secure the significant data. Also, it is easy to avoid making an expensive collection of irrelevant determinations.

For example, the significant chemical criteria in the case of a metal plating waste believed to have killed fish are likely to be cyanide, toxic metals and possibly acidity or alkalinity. In the case of a milk processing plant being gaged as a stream load factor, the general sanitary criteria will evaluate the waste. In the case of a waste being considered as a source of phenolic materials, and as a factor in a stream oxygen sag, phenol, O.C., and B.O.D. along with some other specialized tests may be sufficient. The Fluoride determination, which is rarely applied to industrial wastes, would be a key determination in the examination of fluorination wastes, or processes involving the use of hydrofluoric acid.

In the case of the examples cited, the proper analytical approach has been fairly obvious. This is not always the situation. There is no substitute for experience in designing a procedure for the examination of industrial wastes in connection with a particular situation.

After the objectives of the examination of an industrial waste are fixed, it must be recognized that the task which remains is likely to be a research problem of some magnitude. Analytical methods have an unfortunate tendency to break down when applied to industrial wastes. This is especially true when it is desired to determine a definite component of the waste. When one particular material is involved, it is frequently advisable to take steps to see if the procedure used actually did work.

Suppose it is desired to determine the amount of cyanide present in a given waste sample. First, the method to be used is selected and the determination carried out. Then, as a check on the efficiency of the applied method, a definite amount of cyanide is added to the waste, and a second cyanide determination is made. Unless the difference in the two values obtained is approximately equal to the amount of cyanide added, there is good reason to doubt the method used.

For instance, if (1) analytical results indicate 100 p.p.m.

of cyanide to be present in a given waste and (2) 100 p.p.m. of cyanide are added to a portion of the waste and the fortified portion is analyzed, using the previously applied procedure, the value obtained should be about 200 p.p.m. In the situation just cited, if the second cyanide determination had shown 120 p.p.m. of cyanide present, there would be every reason to reconsider the applicability of the technique used. No analytical method can ever be considered satisfactory unless it will consistently show recovery of a very high percentage of an added amount of the material which it is desired to determine.

No attempt will be made to describe means for determining the presence of materials which give a positive interference with an analytical method applied to an industrial waste. Such a discussion is beyond the scope of this paper. However, one point cannot be over emphasized - - - continued skeptical evaluation of analytical procedures is a "must" if reliable results are to be obtained.

SUMMARY

1. The regular laboratory procedures which may be applied to industrial wastes consist of:
   (a) The general sanitary procedures.
   (b) Procedures established as an integral part of standards.

(c) Procedures specifically designed to gain desired information concerning a particular waste.

2. The successful application of analytical techniques to industrial wastes requires:

(a) Establishment of the purposes to be served by the information to be obtained.

(b) Careful specification of the determinations to be made and the procedures to be followed.

(c) Repeated examinations of the efficiency of analytical procedures to insure that the analytical values are reliable.

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